Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Laser flash photolysis of nanocrystalline α-azido-*p*-methoxyacetophenone

Sujan K. Sarkar,[a] DeVonna M. Gatlin,[a] Anushree Das,[a] Breyinn Loftin,[a] Jeanette A. Krause,[a] Manabu Abe[b] and Anna D. Gudmundsdottir[a]

Contents

1. Characterization of azide 1 and product 7

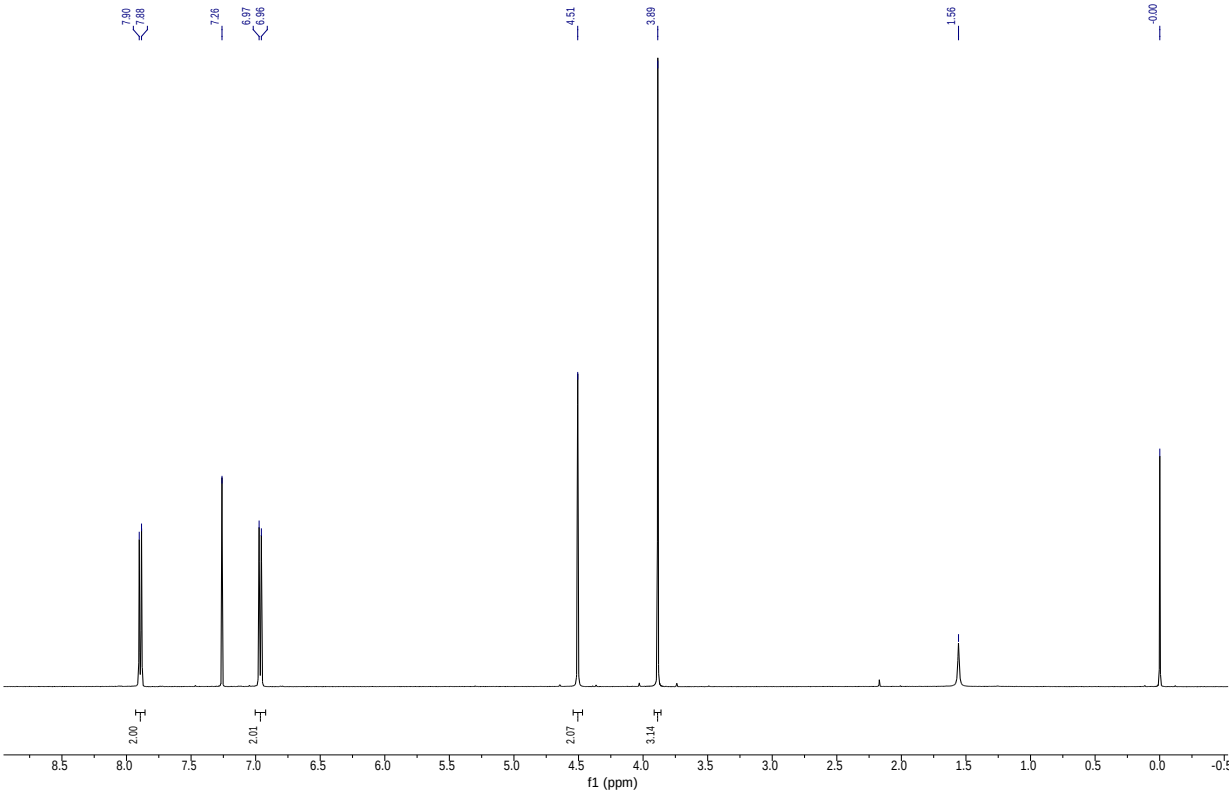


Figure S1. ^{1}H-NMR spectrum of azide **1**.

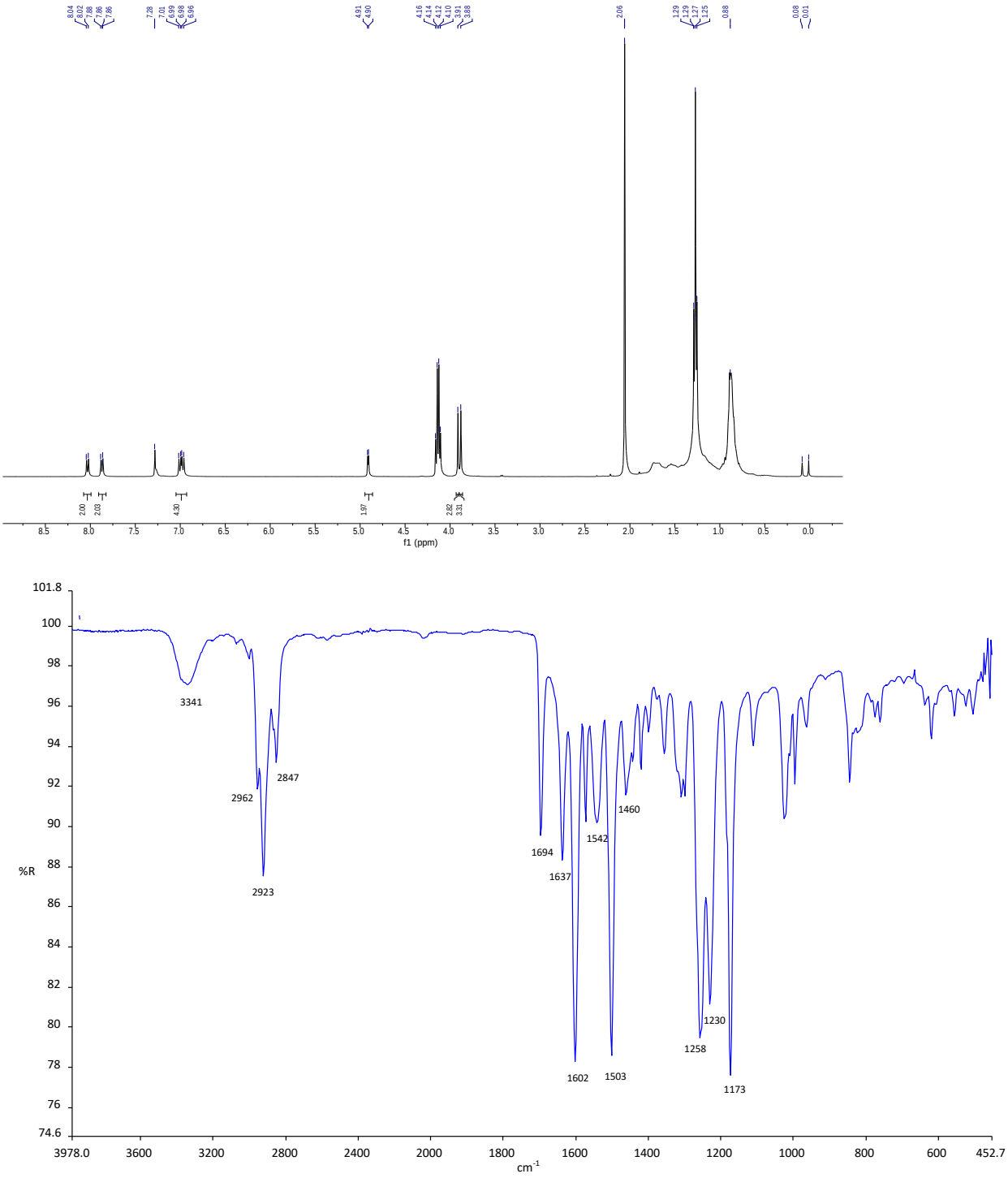


Figure S2. ^{1}H-NMR and IR spectra of product **7**

2. Photos of Crystals of azide 1 before and after irradiation.

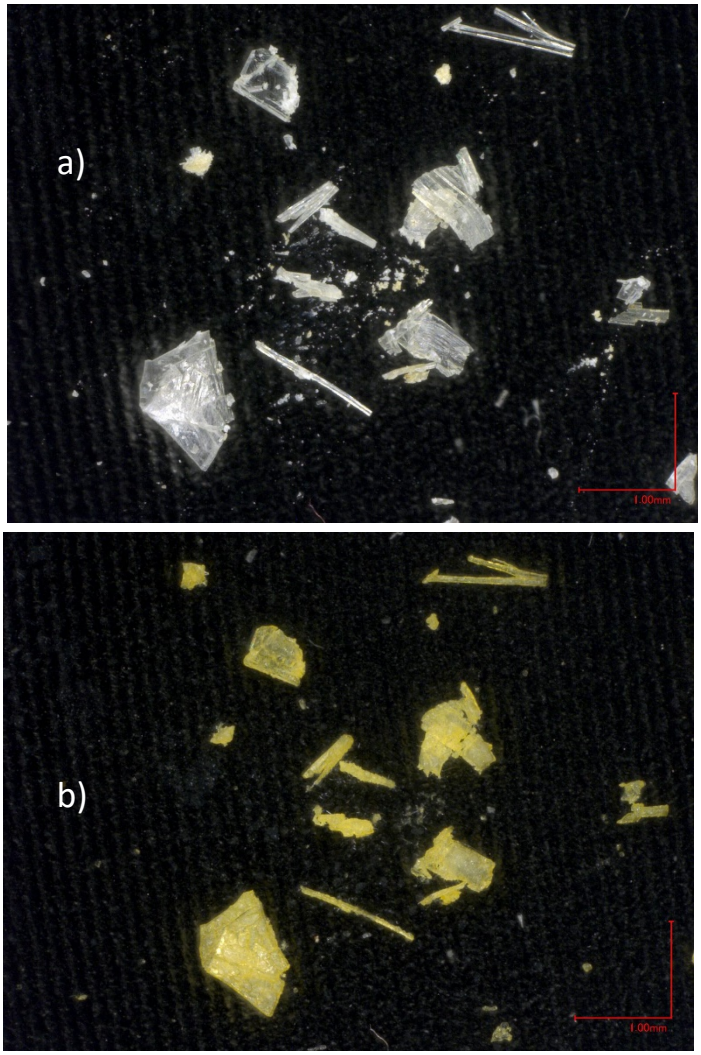
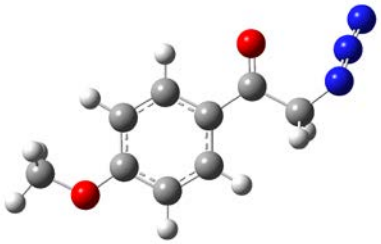


Figure S3. Crystals of azide **1** 1a) before and b) after irradiation with mercury arc lamp through Pyrex filter. The scale is shown in the lower right corners of the figures

3. Molecular modeling

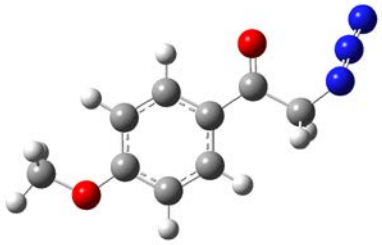
3.1. Optimization of 1A



DFT/B3LYP 6-31+G(d), E = -663.02209626 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.603269	-1.262126	-0.024608
2	6	0	-0.007680	0.007822	0.118925
3	6	0	-0.845452	1.133340	0.165287
4	6	0	-2.229502	1.013094	0.075456
5	6	0	-2.805352	-0.260389	-0.068087
6	6	0	-1.980668	-1.397857	-0.118498
7	1	0	0.006089	-2.159980	-0.066990
8	1	0	-0.389510	2.112592	0.274176
9	1	0	-2.845315	1.904364	0.116594
10	1	0	-2.444857	-2.372843	-0.230294
11	6	0	-5.041299	0.608101	-0.122300
12	1	0	-4.859712	1.300911	-0.953180
13	1	0	-6.037840	0.175299	-0.219058
14	1	0	-4.964763	1.143737	0.831906
15	8	0	1.957421	1.326033	0.323760
16	8	0	-4.139149	-0.495248	-0.166287
17	6	0	1.461290	0.214012	0.217790
18	6	0	2.377762	-1.022584	0.149871
19	1	0	2.040339	-1.784238	0.857015
20	1	0	2.300562	-1.459783	-0.858936
21	7	0	3.767754	-0.750970	0.506304
22	7	0	5.092257	0.739650	-0.778891
23	7	0	4.381966	0.053204	-0.209418

3.2. TD-DFT calculation on 1A



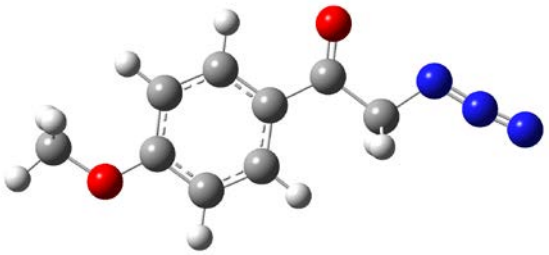
Singlet

```
-----------------------------------------------------------------------
Excitation energies and oscillator strengths:

 Excited State   1:      Singlet-A      3.7905 eV  327.09 nm  f=0.0007
<S**2>=0.000
      48 -> 51         0.32377
      49 -> 51         0.56214
      50 -> 51         0.23515

 Excited State   2:      Singlet-A      4.3142 eV  287.38 nm  f=0.0033
<S**2>=0.000
      48 -> 51        -0.22682
      48 -> 52        -0.17451
      49 -> 52         0.52539
      49 -> 53         0.11203
      50 -> 51         0.11109
      50 -> 52         0.29833

 Excited State   3:      Singlet-A      4.4608 eV  277.94 nm  f=0.1904
<S**2>=0.000
      48 -> 51        -0.39077
      49 -> 52        -0.21097
      50 -> 51         0.51354
      50 -> 52        -0.10120
-----------------------------------------------------------------------
```

Triplet

```
-----------------------------------------------------------------------
Excitation energies and oscillator strengths:

 Excited State   1:      Triplet-A      3.1107 eV  398.57 nm  f=0.0000
<S**2>=2.000
      45 -> 51        -0.11786
      47 -> 53        -0.15230
      49 -> 51        -0.22012
      50 -> 51         0.62867

 Excited State   2:      Triplet-A      3.3674 eV  368.19 nm  f=0.0000
<S**2>=2.000
      47 -> 51        -0.10768
      48 -> 51         0.41024
      49 -> 51         0.50886
      50 -> 51         0.15990

 Excited State   3:      Triplet-A      3.8086 eV  325.54 nm  f=0.0000
<S**2>=2.000
      48 -> 51        -0.10208
      48 -> 52        -0.22523
      49 -> 52         0.54611
      49 -> 53         0.11309
      50 -> 52         0.29484
```

3.3. Optimization of azide 1C



DFT/UB3LYP 6-31+G(d), E = -663.01815909 a.u.

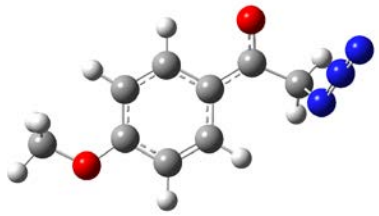
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.471615	-1.044607	0.000060
2	6	0	0.095535	0.314129	0.000024
3	6	0	1.110482	1.283214	0.000012
4	6	0	2.456648	0.927049	0.000023
5	6	0	2.812451	-0.431760	0.000026
6	6	0	1.808608	-1.415697	0.000054
7	1	0	-0.278600	-1.830069	0.000084
8	1	0	0.823776	2.330330	0.000007
9	1	0	3.213321	1.703496	0.000031
10	1	0	2.103661	-2.460496	0.000072
11	6	0	5.163178	0.045771	-0.000122
12	1	0	5.137444	0.676162	0.897307
13	1	0	6.075512	-0.552124	-0.000222
14	1	0	5.137197	0.676098	-0.897587
15	8	0	-1.614777	1.960515	0.000048
16	8	0	4.090226	-0.893001	0.000052
17	6	0	-1.320928	0.777147	0.000011
18	6	0	-2.413308	-0.300119	-0.000065
19	1	0	-2.286390	-0.939658	-0.886402
20	1	0	-2.286411	-0.939811	0.886150
21	7	0	-3.734450	0.337875	0.000003
22	7	0	-5.655749	-1.054519	-0.000025
23	7	0	-4.688199	-0.445469	-0.000033

3.4. TD-DFT calculation for azide 1A

Triplet

```
Excited State   1:      Triplet-A      3.1271 eV  396.48 nm  f=0.0000
<S**2>=2.000
      45 -> 51        -0.12025
      47 -> 53         0.16478
      49 -> 51        -0.10116
      50 -> 51         0.65765
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -662.903240254
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:      Triplet-A      3.3999 eV  364.67 nm  f=0.0000
<S**2>=2.000
      48 -> 51         0.68552
      48 -> 59        -0.14843

 Excited State   3:      Triplet-A      3.8047 eV  325.87 nm  f=0.0000
<S**2>=2.000
      49 -> 52         0.65232
      50 -> 52         0.21559
 SavETr:  write IOETrn=   770 NScale= 10 NData=  16 NLR=1 NState=    3
LETran=      64.
```

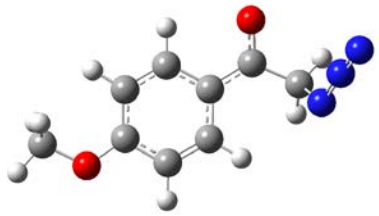
3.5. Optimization of T_1 of 1A



DFT/UB3LYP 6-31+G(d), E = -662.91515691 a.u.
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.357156	1.053282	0.416475
2	6	0	0.086142	-0.308469	0.414557
3	6	0	-0.884817	-1.317406	0.108227
4	6	0	-2.216313	-0.997116	-0.107919
5	6	0	-2.634554	0.344913	-0.048474
6	6	0	-1.683903	1.362991	0.219222
7	1	0	0.357254	1.855459	0.570357
8	1	0	-0.567221	-2.354236	0.089577
9	1	0	-2.925400	-1.793489	-0.305866
10	1	0	-2.027822	2.392886	0.246351
11	6	0	-4.920519	-0.179275	-0.554475
12	1	0	-5.044058	-0.912633	0.252169
13	1	0	-5.840629	0.394923	-0.670325
14	1	0	-4.687250	-0.696025	-1.493528
15	8	0	1.845077	-1.830385	0.161216
16	8	0	-3.911304	0.773372	-0.229923
17	6	0	1.449447	-0.676305	0.640774
18	6	0	2.530143	0.275622	1.090717
19	1	0	2.106915	1.014342	1.774242
20	1	0	3.313761	-0.280437	1.617899
21	7	0	3.136151	1.074522	-0.021682
22	7	0	4.811754	0.070889	-1.374199
23	7	0	3.999730	0.495430	-0.690669

3.6. TD-DFT calculation of T1 of 1A

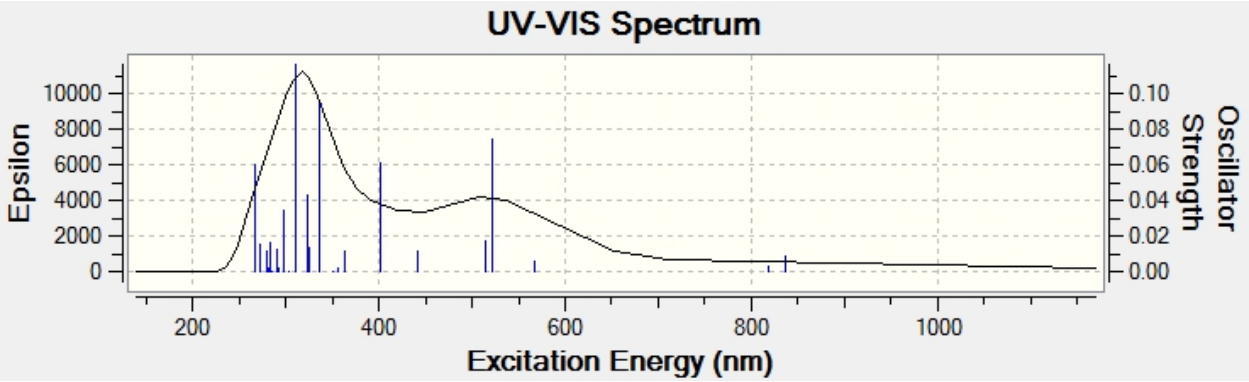


```
 Excited State   1:  3.012-A      0.4642 eV 2671.07 nm  f=0.0163
<S**2>=2.018
     51A -> 54A       -0.11694
     43B -> 50B       -0.13082
     45B -> 50B        0.24820
     46B -> 50B        0.15340
     48B -> 50B        0.16383
     49B -> 50B        0.91607
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -662.898098827
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:  3.020-A      1.4824 eV  836.38 nm  f=0.0084
<S**2>=2.030
     45B -> 50B        0.14787
     47B -> 50B        0.22514
     48B -> 50B        0.91564
     49B -> 50B       -0.22314

 Excited State   3:  3.020-A      1.5154 eV  818.17 nm  f=0.0033
<S**2>=2.031
     45B -> 50B       -0.11522
     47B -> 50B        0.95300
     48B -> 50B       -0.15738
     49B -> 50B        0.15546

 Excited State   4:  3.018-A      2.1891 eV  566.37 nm  f=0.0057
<S**2>=2.027
     51A -> 52A        0.36623
     51A -> 54A        0.17157
     43B -> 50B       -0.31227
     45B -> 50B        0.45768
     46B -> 50B        0.61274
     47B -> 50B        0.14958
     48B -> 50B       -0.26623
     49B -> 50B       -0.16127

 Excited State   5:  3.026-A      2.3779 eV  521.39 nm  f=0.0748
<S**2>=2.039
     51A -> 52A        0.77749
```

```
     51A -> 53A        0.46119
     51A -> 54A       -0.12567
     43B -> 50B        0.12739
     45B -> 50B       -0.24749
     46B -> 50B       -0.18398
     49B -> 50B        0.16346

 Excited State   6:  3.025-A      2.4065 eV  515.21 nm  f=0.0175
<S**2>=2.038
     51A -> 52A       -0.45381
     51A -> 53A        0.86339
     45B -> 50B        0.10732

 Excited State   7:  3.021-A      2.8077 eV  441.59 nm  f=0.0114
<S**2>=2.031
     51A -> 52A       -0.10356
     51A -> 54A       -0.20805
     51A -> 56A        0.14735
     43B -> 50B        0.18419
     45B -> 50B       -0.58422
     46B -> 50B        0.72072

 Excited State   8:  3.049-A      3.0864 eV  401.72 nm  f=0.0611
<S**2>=2.074
     48A -> 53A       -0.10995
     51A -> 54A        0.75863
     51A -> 55A        0.12171
     51A -> 56A       -0.10884
     45B -> 50B       -0.28628
     49B -> 50B        0.11911
     49B -> 51B        0.48997

 Excited State   9:  3.066-A      3.4128 eV  363.29 nm  f=0.0114
<S**2>=2.100
     51A -> 54A        0.32591
     51A -> 56A        0.86517
     44B -> 50B        0.16052
     49B -> 51B       -0.19436

 Excited State  10:  3.021-A      3.4793 eV  356.35 nm  f=0.0016
<S**2>=2.031
     51A -> 56A       -0.16633
     41B -> 50B       -0.18481
     42B -> 50B        0.22204
     44B -> 50B        0.92439

 Excited State  11:  3.018-A      3.5390 eV  350.33 nm  f=0.0004
<S**2>=2.026
     51A -> 54A       -0.15901
     51A -> 55A        0.91865
     51A -> 57A        0.31652
```

```
 Excited State  12:  3.091-A      3.6794 eV  336.97 nm  f=0.0941
<S**2>=2.139
     48A -> 53A        0.10854
     51A -> 54A       -0.14458
     40B -> 50B        0.20711
     43B -> 50B        0.70377
     45B -> 50B        0.36657
     46B -> 50B        0.11016
     48B -> 52B       -0.11765
     49B -> 51B        0.44584

 Excited State  13:  3.540-A      3.8037 eV  325.96 nm  f=0.0132
<S**2>=2.883
     49A -> 52A        0.27575
     50A -> 52A       -0.27244
     51A -> 54A        0.14502
     51A -> 55A       -0.16288
     51A -> 57A        0.49248
     40B -> 50B        0.10286
     43B -> 50B        0.31737
     45B -> 50B        0.11270
     48B -> 51B        0.26996
     48B -> 52B        0.31131
     49B -> 51B       -0.28405
     49B -> 52B       -0.32575

 Excited State  14:  3.182-A      3.8272 eV  323.95 nm  f=0.0434
<S**2>=2.281
     49A -> 52A       -0.12848
     50A -> 52A        0.11463
     51A -> 54A       -0.14307
     51A -> 55A       -0.29228
     51A -> 56A        0.14316
     51A -> 57A        0.76478
     43B -> 50B       -0.16991
     48B -> 51B       -0.13787
     48B -> 52B       -0.20203
     49B -> 51B        0.27568
     49B -> 52B        0.18624

 Excited State  15:  3.413-A      3.9881 eV  310.89 nm  f=0.1160
<S**2>=2.663
     49A -> 52A        0.25715
     49A -> 54A       -0.10393
     50A -> 52A       -0.29271
     51A -> 54A       -0.28581
     51A -> 56A        0.23663
     51A -> 57A       -0.13297
     51A -> 60A       -0.10803
     51A -> 61A        0.12811
     41B -> 50B       -0.31176
     43B -> 50B       -0.24949
```

```
      48B -> 51B         0.19505
      48B -> 52B         0.22386
      48B -> 55B         0.11386
      49B -> 50B        -0.10391
      49B -> 51B         0.43826
      49B -> 52B        -0.23822

 Excited State  16:  3.017-A      4.0928 eV  302.93 nm  f=0.0001
<S**2>=2.026
      51A -> 58A         0.97119
      51A -> 59A        -0.11518
      51A -> 63A         0.13483
```



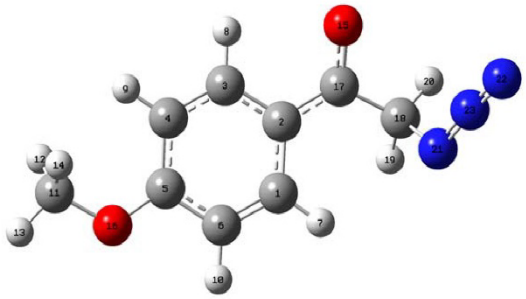
3.7. Spin density calculation of T1 of 1A

Natural

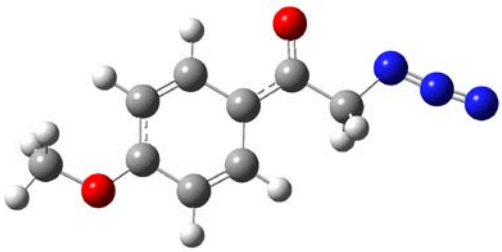
Atom	No	Charge	Core	Valence	Rydberg	Total
C	1	-0.17529	0.99955	2.16768	0.00806	3.17529
C	2	-0.07528	0.9995	2.0664	0.00938	3.07528
C	3	-0.20761	0.99957	2.19814	0.00991	3.20761
C	4	-0.1188	0.99952	2.1121	0.00719	3.1188
C	5	0.05236	0.99943	1.93635	0.01185	2.94764
C	6	-0.11329	0.99953	2.10536	0.0084	3.11329
H	7	0.1274	0	0.37193	0.00067	0.3726
H	8	0.13451	0	0.36487	0.00062	0.36549
H	9	0.12303	0	0.37655	0.00041	0.37697
H	10	0.12877	0	0.37063	0.0006	0.37123
C	11	-0.16238	0.99975	2.15513	0.0075	3.16238
H	12	0.10513	0	0.39411	0.00076	0.39487
H	13	0.12059	0	0.37929	0.00011	0.37941
H	14	0.10575	0	0.39343	0.00081	0.39425
O	15	-0.58864	0.99993	3.58035	0.00837	4.58864
O	16	-0.29513	0.99987	3.28542	0.00985	4.29513
C	17	-0.08608	0.99952	2.06835	0.01821	3.08608
C	18	-0.18334	0.99962	2.17259	0.01112	3.18334
H	19	0.13035	0	0.36928	0.00038	0.36965
H	20	0.12562	0	0.37335	0.00103	0.37438
N	21	-0.19624	0.99972	2.68142	0.0151	3.69624
N	22	-0.06043	0.99984	2.54698	0.01362	3.56043
N	23	0.10902	0.99979	2.37426	0.01693	3.39098

Natural

Atom	No	Charge	Core	Valence	Rydberg	Total	Spin Density
C	1	-0.05139	0.99955	2.04467	0.00717	3.05139	-0.1239
C	2	-0.00489	0.99947	1.99774	0.00768	3.00489	-0.07039
C	3	0.00439	0.99956	1.98793	0.00811	2.99561	-0.212
C	4	-0.19515	0.99952	2.18859	0.00705	3.19515	0.07635
C	5	0.26996	0.99943	1.71937	0.01123	2.73004	-0.2176
C	6	-0.13058	0.99953	2.12289	0.00816	3.13058	0.01729
H	7	0.12342	0	0.37589	0.00069	0.37658	0.00398
H	8	0.12743	0	0.37189	0.00068	0.37257	0.00708
H	9	0.12531	0	0.37427	0.00042	0.37469	-0.00228
H	10	0.12966	0	0.36974	0.0006	0.37034	-0.00089
C	11	-0.16649	0.99975	2.15941	0.00733	3.16649	0.00411
H	12	0.1095	0	0.38992	0.00058	0.3905	-0.00437
H	13	0.12052	0	0.37937	0.00011	0.37948	7E-05
H	14	0.10983	0	0.38958	0.00059	0.39017	-0.00408
O	15	0.25232	0.99993	2.74272	0.00503	3.74768	-0.84096
O	16	-0.21885	0.99987	3.20965	0.00933	4.21885	-0.07628
C	17	0.33101	0.99952	1.65396	0.01551	2.66899	-0.41709
C	18	-0.15334	0.99959	2.14502	0.00873	3.15334	-0.03
H	19	0.13697	0	0.36253	0.0005	0.36303	-0.00662
H	20	0.13054	0	0.36866	0.0008	0.36946	-0.00492
N	21	-0.15598	0.99972	2.64221	0.01405	3.65598	-0.04026
N	22	0.00326	0.99984	2.4839	0.01301	3.49674	-0.06369
N	23	0.10253	0.99978	2.38135	0.01634	3.39747	0.00649



3.8. Optimization of T1 of 1C



DFT/UB3LYP 6-31+G(d), -662.90704690 a.u.

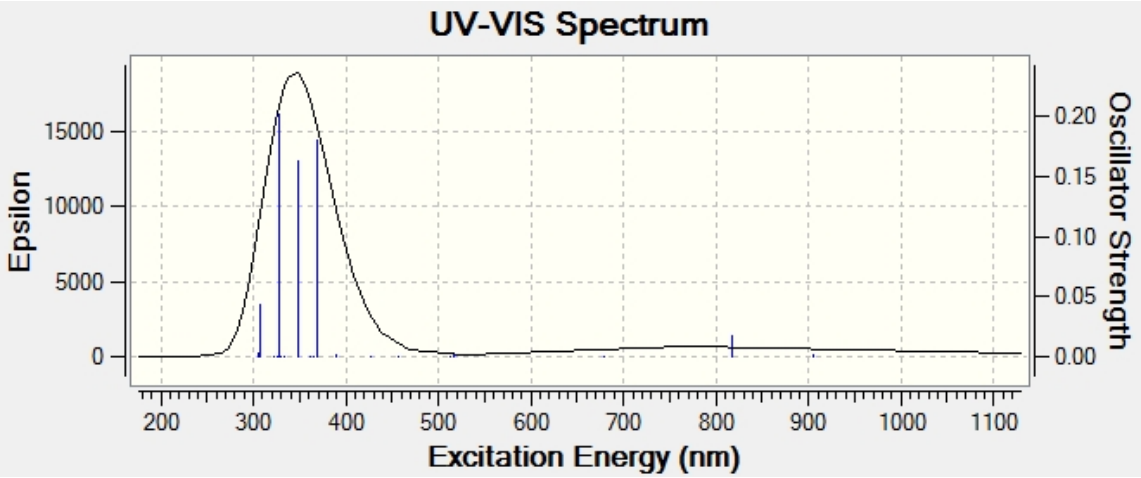
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.471370	-1.103053	-0.000182
2	6	0	0.053931	0.296838	-0.000087
3	6	0	1.127123	1.323415	0.000021
4	6	0	2.446513	0.970390	0.000108
5	6	0	2.817296	-0.406063	0.000058
6	6	0	1.788922	-1.432979	-0.000086
7	1	0	-0.274771	-1.890636	-0.000332
8	1	0	0.814520	2.360212	0.000056
9	1	0	3.207884	1.743859	0.000225
10	1	0	2.115261	-2.469146	-0.000142
11	6	0	5.179369	0.032583	-0.000048
12	1	0	5.159898	0.660479	0.897941
13	1	0	6.077081	-0.585964	-0.000255
14	1	0	5.159442	0.660442	-0.898049
15	8	0	-1.583032	1.960904	-0.000023
16	8	0	4.081699	-0.883727	0.000254
17	6	0	-1.303635	0.729772	-0.000081
18	6	0	-2.412296	-0.326886	-0.000168
19	1	0	-2.316868	-0.975860	-0.886024
20	1	0	-2.316802	-0.976069	0.885523
21	7	0	-3.722886	0.339537	-0.000061
22	7	0	-5.673927	-1.010406	0.000246
23	7	0	-4.692692	-0.421823	0.000100

3.9. TD-DFT calculations for T_1 of 1C

```
Excitation energies and oscillator strengths:

 Excited State   1:  3.016-A      0.4917 eV 2521.61 nm  f=0.0000
<S**2>=2.024
     49B -> 50B        0.98274
     49B -> 51B        0.17479
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -662.888977780
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:  3.048-A      1.3703 eV  904.77 nm  f=0.0020
<S**2>=2.072
     51A -> 52A        0.66583
     47B -> 50B       -0.65488
     48B -> 50B        0.33319

 Excited State   3:  3.020-A      1.5165 eV  817.56 nm  f=0.0176
<S**2>=2.030
     51A -> 52A       -0.29879
     47B -> 50B        0.16311
     48B -> 50B        0.93743

 Excited State   4:  3.015-A      1.8235 eV  679.92 nm  f=0.0009
<S**2>=2.023
     51A -> 52A        0.67131
     47B -> 50B        0.73261

 Excited State   5:  3.032-A      2.4032 eV  515.91 nm  f=0.0040
<S**2>=2.048
     47A -> 52A       -0.10076
     51A -> 55A        0.53908
     51A -> 58A       -0.29863
     45B -> 50B        0.76542

 Excited State   6:  3.023-A      2.4198 eV  512.38 nm  f=0.0002
<S**2>=2.035
     51A -> 53A        0.99644

 Excited State   7:  3.018-A      2.7111 eV  457.31 nm  f=0.0000
<S**2>=2.028
     44B -> 50B        0.11461
     46B -> 50B        0.99069

 Excited State   8:  3.020-A      2.9105 eV  425.98 nm  f=0.0008
<S**2>=2.031
     51A -> 54A        0.95991
     51A -> 56A        0.23578
```

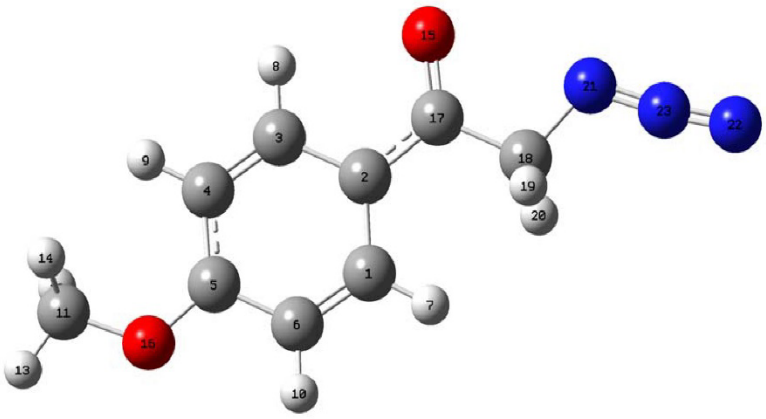
```
 Excited State   9:  3.022-A      3.1886 eV  388.84 nm  f=0.0024
<S**2>=2.033
     51A -> 54A       -0.23572
     51A -> 56A        0.96481

 Excited State  10:  3.049-A      3.3566 eV  369.37 nm  f=0.1802
<S**2>=2.074
     47A -> 52A        0.14068
     51A -> 55A        0.76144
     51A -> 58A        0.38222
     43B -> 50B       -0.27681
     45B -> 50B       -0.38436

 Excited State  11:  3.022-A      3.3930 eV  365.42 nm  f=0.0000
<S**2>=2.033
     44B -> 50B        0.97239
     46B -> 50B       -0.11679
     49B -> 51B       -0.12195

 Excited State  12:  3.019-A      3.4319 eV  361.27 nm  f=0.0006
<S**2>=2.029
     51A -> 57A        0.97059
     51A -> 60A        0.16524

 Excited State  13:  3.055-A      3.5609 eV  348.19 nm  f=0.1625
<S**2>=2.084
     47A -> 52A       -0.16968
     51A -> 58A        0.68089
     51A -> 71A        0.11232
     43B -> 50B        0.61672
     45B -> 50B        0.25412

 Excited State  14:  3.022-A      3.7138 eV  333.85 nm  f=0.0000
<S**2>=2.033
     51A -> 57A       -0.17244
     51A -> 59A       -0.13386
     51A -> 60A        0.95557
     51A -> 64A        0.15099

 Excited State  15:  3.118-A      3.7638 eV  329.41 nm  f=0.0000
<S**2>=2.181
     44B -> 50B        0.12983
     49B -> 50B       -0.18208
     49B -> 51B        0.93132
     49B -> 61B       -0.14317
     49B -> 64B       -0.13416

 Excited State  16:  3.043-A      3.7801 eV  327.99 nm  f=0.2020
<S**2>=2.065
     51A -> 55A        0.31886
     51A -> 58A       -0.51077
     51A -> 61A        0.20654
```

```
     51A -> 71A         0.12591
     41B -> 50B        -0.18812
     43B -> 50B         0.57794
     45B -> 50B        -0.37295
     47B -> 53B         0.12495

 Excited State  17:  4.119-A      3.7954 eV  326.67 nm  f=0.0000
<S**2>=3.992
     48A -> 53A         0.11345
     50A -> 53A        -0.67916
     48B -> 52B         0.68916

 Excited State  18:  3.022-A      3.8382 eV  323.03 nm  f=0.0006
<S**2>=2.033
     51A -> 54A        -0.10930
     51A -> 59A         0.97174
     51A -> 60A         0.12725

 Excited State  19:  3.107-A      4.0287 eV  307.76 nm  f=0.0441
<S**2>=2.164
     50A -> 55A         0.11283
     50A -> 58A         0.12186
     51A -> 61A         0.92362
     51A -> 63A        -0.17806
     43B -> 50B        -0.12822
     48B -> 56B         0.16036

 Excited State  20:  4.048-A      4.0620 eV  305.23 nm  f=0.0033
<S**2>=3.847
     46A -> 53A         0.25442
     50A -> 55A         0.39706
     50A -> 58A         0.45183
     51A -> 58A        -0.10961
     51A -> 61A        -0.24384
     46B -> 52B        -0.25591
     48B -> 56B         0.60173
```

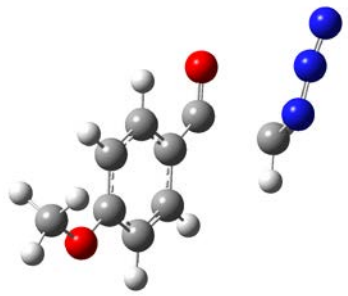


3.10. Spin density calculation for T_1 of 1C

Natural	#VALUE!							Natural							
	Atom	No	Charge	Core	Valence	Rydberg	Total		Atom	No	Charge	Core	Valence	Rydberg	Total	**Calculated Spin Density**
		0														
	C	1	-0.17078	0.99956	2.162	0.00923	3.17078		C	1	-0.10512	0.99956	2.09854	0.00702	3.10512	-0.06566
	C	2	-0.23076	0.99952	2.22206	0.00917	3.23076		C	2	0.24452	0.99951	1.7484	0.00757	2.75548	-0.47528
	C	3	-0.2618	0.99958	2.24908	0.01314	3.2618		C	3	0.04124	0.99957	1.95052	0.00866	2.95876	-0.30304
	C	4	-0.11841	0.99952	2.11161	0.00729	3.11841		C	4	-0.18661	0.99952	2.18028	0.00682	3.18661	0.0682
	C	5	-0.07229	0.99949	2.05966	0.01313	3.07229		C	5	0.38653	0.99949	1.60301	0.01098	2.61347	-0.45882
	C	6	-0.16308	0.99954	2.15368	0.00987	3.16308		C	6	-0.03695	0.99954	2.02941	0.008	3.03695	-0.12613
	H	7	0.12549	0	0.37407	0.00044	0.37451		H	7	0.1223	0	0.37723	0.00047	0.3777	0.00319
	H	8	0.14192	0	0.35743	0.00064	0.35808		H	8	0.13224	0	0.36705	0.00072	0.36776	0.00968
	H	9	0.12449	0	0.3751	0.00041	0.37551		H	9	0.1256	0	0.37397	0.00043	0.3744	-0.00111
	H	10	0.13155	0	0.36791	0.00053	0.36845		H	10	0.12725	0	0.37219	0.00056	0.37275	0.0043
	C	11	-0.16151	0.99975	2.15436	0.0074	3.16151		C	11	-0.17053	0.99975	2.16373	0.00705	3.17053	0.00902
	H	12	0.10613	0	0.39302	0.00085	0.39387		H	12	0.1151	0	0.38446	0.00044	0.3849	-0.00897
	H	13	0.12209	0	0.37779	0.00012	0.37791		H	13	0.12189	0	0.37799	0.00013	0.37811	0.0002
	H	14	0.10613	0	0.39302	0.00085	0.39387		H	14	0.1151	0	0.38446	0.00044	0.3849	-0.00897
	O	15	-0.45932	0.99991	3.44827	0.01114	4.45932		O	15	-0.06602	0.99991	3.05747	0.00865	4.06602	-0.3933
	O	16	-0.32346	0.99987	3.31331	0.01029	4.32346		O	16	-0.1593	0.99987	3.15046	0.00897	4.1593	-0.16416
	C	17	0.13157	0.99957	1.85034	0.01852	2.86843		C	17	0.20923	0.99957	1.77362	0.01758	2.79077	-0.07766
	C	18	-0.16964	0.99963	2.16213	0.00787	3.16964		C	18	-0.17585	0.99964	2.16841	0.0078	3.17585	0.00621
	H	19	0.11764	0	0.38128	0.00109	0.38236		H	19	0.12339	0	0.37583	0.00078	0.37661	-0.00575
	H	20	0.11764	0	0.38128	0.00109	0.38236		H	20	0.12338	0	0.37584	0.00078	0.37662	-0.00574
	N	21	-0.15634	0.99969	2.64337	0.01328	3.65634		N	21	-0.15361	0.99969	2.64041	0.01351	3.65361	-0.00273
	N	22	-0.04431	0.99984	2.5306	0.01387	3.54431		N	22	-0.0399	0.99984	2.52623	0.01384	3.5399	-0.00441
	N	23	0.10705	0.99979	2.37629	0.01688	3.39295		N	23	0.10612	0.99979	2.37731	0.01679	3.39388	0.00093

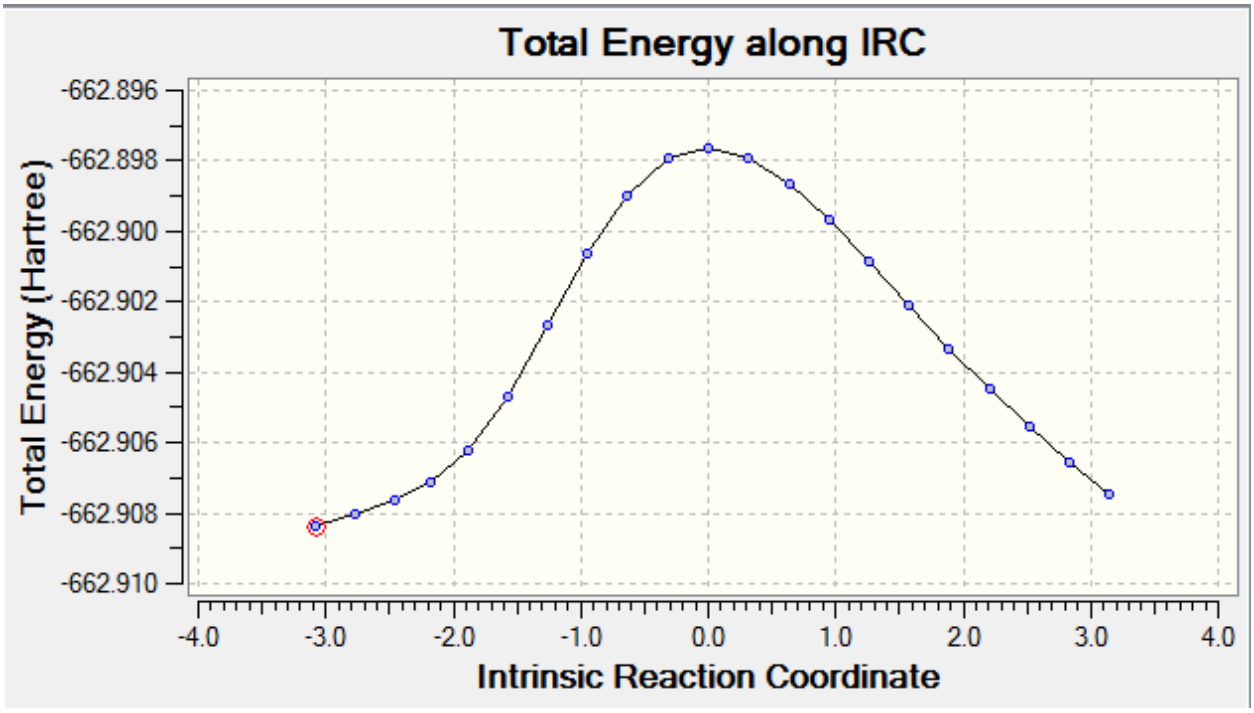


3.11. TS and IRC calculation for forming benzoyl radical 4 and 5 from T_1 of 1

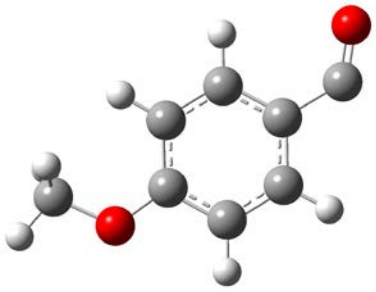


DFT/UB3LYP 6-31+G(d), E = -662.89761649 a.u.
Imaginary frequency = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.648733	1.536360	0.127577
2	6	0	0.080578	0.435278	0.625631
3	6	0	-0.576733	-0.803713	0.740523
4	6	0	-1.915239	-0.946631	0.369824
5	6	0	-2.617924	0.153833	-0.140133
6	6	0	-1.971738	1.399044	-0.258168
7	1	0	-0.174391	2.512629	0.064301
8	1	0	-0.032358	-1.656652	1.134366
9	1	0	-2.393404	-1.913689	0.481194
10	1	0	-2.536666	2.243890	-0.640565
11	6	0	-4.638753	-1.100442	-0.443814
12	1	0	-4.696595	-1.449766	0.595128
13	1	0	-5.643028	-0.883990	-0.811413
14	1	0	-4.179445	-1.877047	-1.068812
15	8	0	2.161757	-0.303028	1.629493
16	8	0	-3.922511	0.125804	-0.535958
17	6	0	1.458372	0.583585	1.132700
18	6	0	2.545011	1.208906	-0.386481
19	1	0	1.879575	1.896812	-0.894422
20	1	0	3.344715	1.651199	0.205511
21	7	0	2.862429	0.126422	-1.191754
22	7	0	4.560022	-1.450896	-0.636038
23	7	0	3.753061	-0.661656	-0.803568


Total Energy along IRC
Total Energy (Hartree)
-662.896
-662.898
-662.900
-662.902
-662.904
-662.906
-662.908
-662.910
-4.0
-3.0
-2.0
-1.0
0.0
1.0
2.0
3.0
4.0
Intrinsic Reaction Coordinate

3.12. Optimization of benzoyl radical 4



DFT/UB3LYP 6-31+G(d), E = -459.46643887 a.u.
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.842659	1.431114	-0.000010
2	6	0	-1.524771	0.200197	-0.000031
3	6	0	-0.783405	-0.994529	-0.000012
4	6	0	0.608377	-0.968162	-0.000010
5	6	0	1.277208	0.269641	0.000007
6	6	0	0.543184	1.469697	0.000017
7	1	0	-1.417376	2.353281	-0.000024
8	1	0	-1.309644	-1.945061	-0.000004
9	1	0	1.160878	-1.901103	-0.000013
10	1	0	1.085014	2.410364	0.000031
11	6	0	3.445716	-0.760015	-0.000002
12	1	0	3.270325	-1.365599	-0.897644
13	1	0	4.474181	-0.396670	0.000007
14	1	0	3.270322	-1.365628	0.897620
15	8	0	-3.740947	-0.754028	0.000041
16	8	0	2.627664	0.407869	0.000015
17	6	0	-2.994889	0.182006	-0.000027

3.13. TD-DFT calculation for benzoyl radical 4

```
Excitation energies and oscillator strengths:

 Excited State   1:  2.007-A      1.8075 eV  685.93 nm  f=0.0007
<S**2>=0.757
     36A -> 37A        0.97890
     36A -> 42A        0.15374
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -459.400013212
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:  3.463-A      3.2470 eV  381.84 nm  f=0.0005
<S**2>=2.748
     33A -> 37A       -0.10734
     34A -> 38A       -0.19030
     35A -> 37A        0.68591
     33B -> 37B       -0.10020
     34B -> 38B        0.18534
     35B -> 37B        0.64558

 Excited State   3:  2.015-A      3.5612 eV  348.15 nm  f=0.0000
<S**2>=0.765
     36A -> 38A        0.99687

 Excited State   4:  2.033-A      3.9790 eV  311.60 nm  f=0.0000
<S**2>=0.783
     33B -> 36B       -0.14896
     35B -> 36B        0.98394

 Excited State   5:  3.454-A      4.2428 eV  292.22 nm  f=0.0008
<S**2>=2.733
     34A -> 37A        0.58663
     34A -> 38A       -0.26797
     35A -> 37A       -0.13854
     35A -> 38A       -0.31108
     34B -> 37B        0.48043
     34B -> 38B        0.27372
     35B -> 38B        0.36715

 Excited State   6:  3.446-A      4.4194 eV  280.55 nm  f=0.0018
<S**2>=2.719
     34A -> 37A        0.49351
     34A -> 38A        0.44874
     35A -> 37A        0.17970
     35A -> 38A        0.29386
     34B -> 37B        0.35619
     34B -> 38B       -0.47076
     35B -> 38B       -0.24657
```

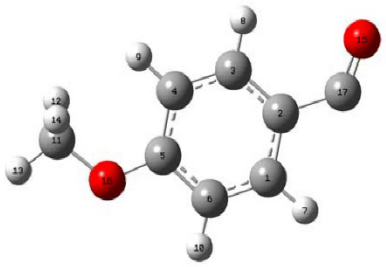
3.14. Spin density calculation of benzoyl radical 4

Natural

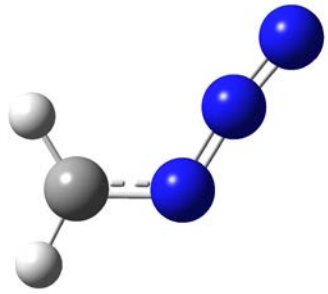
Atom	No	Charge	Core	Valence	Rydberg	Total
C	1	-0.07974	0.99954	2.07159	0.00861	3.07974
C	2	-0.16826	0.99949	2.15327	0.0155	3.16826
C	3	-0.08627	0.99954	2.07769	0.00904	3.08627
C	4	-0.16405	0.99952	2.15729	0.00724	3.16405
C	5	0.17812	0.99943	1.81091	0.01154	2.82188
C	6	-0.14148	0.99952	2.13388	0.00808	3.14148
H	7	0.12561	0	0.37252	0.00187	0.37439
H	8	0.12739	0	0.37076	0.00185	0.37261
H	9	0.12297	0	0.37646	0.00058	0.37703
H	10	0.1296	0	0.36976	0.00064	0.3704
C	11	-0.1644	0.99975	2.15725	0.0074	3.1644
H	12	0.10717	0	0.39219	0.00064	0.39283
H	13	0.12089	0	0.379	0.00011	0.37911
H	14	0.10717	0	0.39219	0.00064	0.39283
O	15	-0.38612	0.9999	3.36949	0.01673	4.38612
O	16	-0.26251	0.99986	3.25299	0.00965	4.26251
C	17	-0.06609	0.99972	2.03071	0.03567	3.06609

Natural

Atom	No	Charge	Core	Valence	Rydberg	Total	Spin Density
C	1	-0.08618	0.99954	2.07959	0.00705	3.08618	0.00644
C	2	-0.09626	0.99939	2.08782	0.00905	3.09626	-0.072
C	3	-0.0751	0.99953	2.06807	0.0075	3.0751	-0.01117
C	4	-0.15983	0.99951	2.15325	0.00707	3.15983	-0.00422
C	5	0.17138	0.99943	1.81773	0.01147	2.82862	0.00674
C	6	-0.13868	0.99952	2.1311	0.00806	3.13868	-0.0028
H	7	0.13001	0	0.36968	0.00031	0.36999	-0.0044
H	8	0.13104	0	0.36852	0.00044	0.36896	-0.00365
H	9	0.12568	0	0.37391	0.00041	0.37432	-0.00271
H	10	0.12949	0	0.36987	0.00064	0.37051	0.00011
C	11	-0.16422	0.99975	2.15708	0.00738	3.16422	-0.00018
H	12	0.10704	0	0.39232	0.00064	0.39296	0.00013
H	13	0.12098	0	0.37892	0.0001	0.37902	-9E-05
H	14	0.10704	0	0.39232	0.00064	0.39296	0.00013
O	15	-0.11485	0.9999	3.10351	0.01144	4.11485	-0.27127
O	16	-0.26486	0.99986	3.25532	0.00967	4.26486	0.00235
C	17	0.57731	0.99943	1.40521	0.01804	2.42269	-0.6434



3.15. Optimization of CH_2N_3 radical 5



DFT/UB3LYP 6-31+G(d), E = -203.44880419 a.u.
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.582450	0.279219	0.000042
2	1	0	2.541316	-0.216963	0.000075
3	1	0	1.488715	1.360532	-0.000174
4	7	0	0.498547	-0.538371	-0.000052
5	7	0	-1.773385	0.207624	0.000001
6	7	0	-0.657267	-0.071949	0.000030

3.16. TD-DFT calculation of CH_2N_3 radical 5

```
Excited State   1:  2.074-A      2.0331 eV  609.82 nm  f=0.0000
<S**2>=0.826
     15A -> 16A        0.99166
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -203.374087795
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:  2.073-A      3.6736 eV  337.50 nm  f=0.0282
<S**2>=0.824
     15A -> 17A        0.88526
     13B -> 16B        0.16056
     14B -> 15B        0.41648

 Excited State   3:  2.037-A      4.4955 eV  275.79 nm  f=0.0224
<S**2>=0.787
     15A -> 18A        0.98371
     15A -> 19A        0.12281

 Excited State   4:  3.429-A      4.7412 eV  261.51 nm  f=0.0043
<S**2>=2.689
     12A -> 16A        0.13678
     14A -> 16A        0.73425
     15A -> 17A        0.14176
     12B -> 16B       -0.11936
     13B -> 16B       -0.60259

 Excited State   5:  2.080-A      4.8554 eV  255.35 nm  f=0.0003
<S**2>=0.831
     15A -> 19A        0.21101
     13B -> 15B        0.95592
     14B -> 16B        0.13050
```

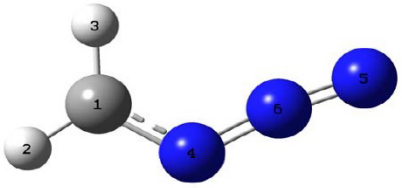
3.17. Spin density calculation for CH_2N_3 radical 5

Natural

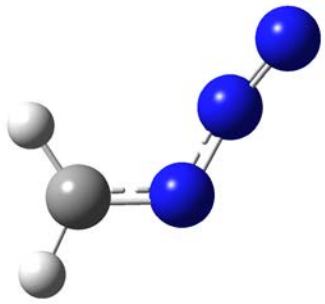
Atom	No	Charge	Core	Valence	Rydberg	Total
C	1	-0.49132	0.99976	2.47049	0.02108	3.49132
H	2	0.12204	0	0.37785	0.00011	0.37796
H	3	0.11133	0	0.38802	0.00065	0.38867
N	4	-0.1156	0.99968	2.6022	0.01372	3.6156
N	5	-0.19037	0.99984	2.67483	0.01569	3.69037
N	6	0.06392	0.99978	2.41946	0.01683	3.43608

Natural

Atom	No	Charge	Core	Valence	Rydberg	Total	SpinDensity
C	1	0.23533	0.99976	1.75354	0.01137	2.76467	0.72665
H	2	0.10048	0	0.39941	0.00011	0.39952	-0.02156
H	3	0.08975	0	0.40959	0.00066	0.41025	-0.02158
N	4	-0.18351	0.99968	2.67165	0.01218	3.68351	-0.06791
N	5	0.14745	0.99984	2.34149	0.01122	3.35255	0.33782
N	6	0.11049	0.99978	2.37385	0.01587	3.38951	0.04657

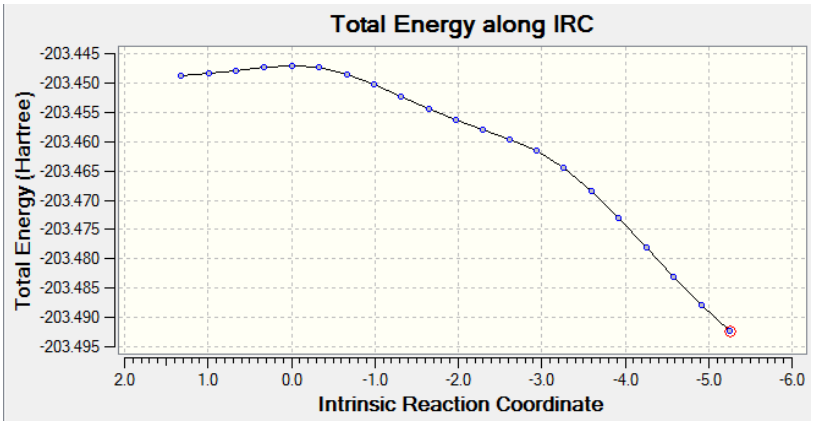


3.18. TS and IRC to form CH_2N radical 6 from radical 5

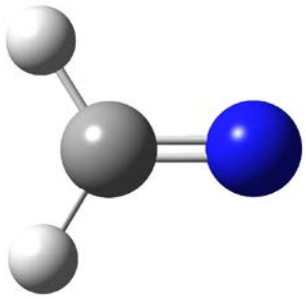


DFT/UB3LYP 6-31+G(d), E = -203.44703849 a.u.
Imaginary frequency = 1
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.564813	0.274071	-0.022607
2	1	0	2.531696	-0.206044	-0.090896
3	1	0	1.478539	1.354472	0.067318
4	7	0	0.512321	-0.529960	-0.041877
5	7	0	-1.761586	0.201129	-0.103402
6	7	0	-0.664894	-0.070149	0.168025



3.19. Optimization of CH_2N radical 6



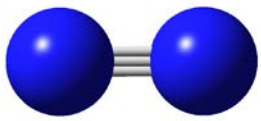
DFT/UB3LYP 6-31+G(d), E = -93.98904087 a.u.
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.505984	0.000000	0.000008
2	1	0	1.081332	-0.938544	0.000159
3	1	0	1.081332	0.938544	-0.000126
4	7	0	-0.742652	0.000000	-0.000011

3.20. TD-DFT for imine radical 6.

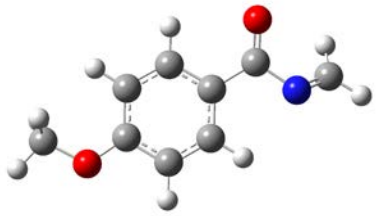
```
Excited State   1:  1.997-A      3.9285 eV  315.60 nm  f=0.0000
<S**2>=0.747
      8A ->  9A        0.51261
      7B ->  8B        0.85437
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -93.8446704080
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:  2.011-A      4.5325 eV  273.54 nm  f=0.0060
<S**2>=0.761
      6B ->  8B        0.99387

 Excited State   3:  2.018-A      4.6122 eV  268.82 nm  f=0.0000
<S**2>=0.768
      8A ->  9A        0.85131
      7B ->  8B       -0.51665
```

3.21. Optimization of N_2



```
DFT/B3LYP 6-31+G(d), E = -109.52977937 a.u.
Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1          7           0        0.000000    0.000000    0.552562
      2          7           0        0.000000    0.000000   -0.552562
 ---------------------------------------------------------------------
```

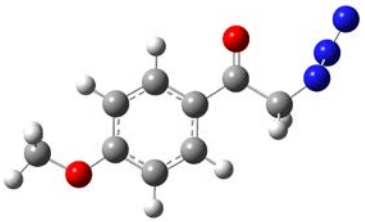
3.22. Optimization of p-MeO-PhCONCH$_2$ 7



DFT/B3LYP 6-31+G(d), E = -553.56854408 a.u.
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.265684	-1.168701	0.198496
2	6	0	0.775611	0.142807	0.125441
3	6	0	-0.124691	1.210693	-0.004525
4	6	0	-1.498807	0.991340	-0.066039
5	6	0	-1.993012	-0.322094	0.004698
6	6	0	-1.100968	-1.400087	0.138631
7	1	0	0.951437	-2.000847	0.315936
8	1	0	0.269088	2.221093	-0.058093
9	1	0	-2.169579	1.836895	-0.168228
10	1	0	-1.505871	-2.405703	0.199656
11	6	0	-4.277913	0.389184	-0.172372
12	1	0	-4.138253	0.948049	-1.106228
13	1	0	-5.247196	-0.111272	-0.188700
14	1	0	-4.235139	1.077510	0.681004
15	8	0	2.689412	1.566522	0.219010
16	8	0	-3.312036	-0.650179	-0.045059
17	6	0	2.227384	0.433659	0.165993
18	7	0	3.069907	-0.719753	0.193898
19	6	0	4.122996	-0.689868	-0.518719
20	1	0	4.817782	-1.529874	-0.474902
21	1	0	4.371686	0.150085	-1.178965

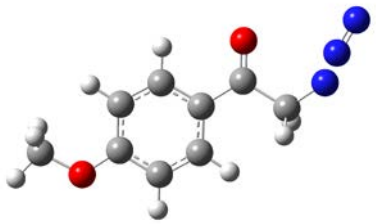
3.23. Optimization of T_A of 1A



DFT/UB3LYP 6-31+G(d), E = -662.95052346 a.u.
Standard orientation:

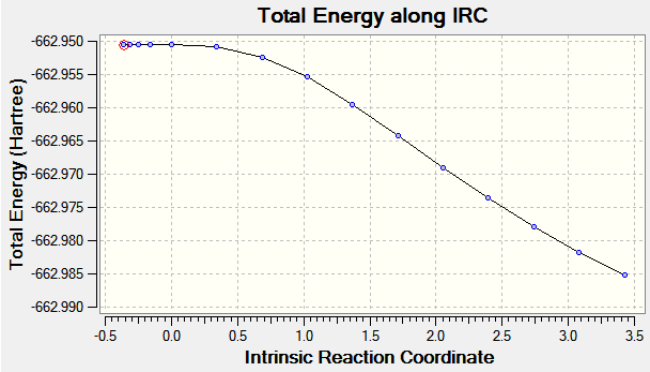
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.598770	1.240064	0.001020
2	6	0	-0.021874	-0.040882	-0.114047
3	6	0	-0.875143	-1.155840	-0.140386
4	6	0	-2.257230	-1.013541	-0.057672
5	6	0	-2.815173	0.270864	0.057890
6	6	0	-1.974062	1.397246	0.087962
7	1	0	0.023382	2.129555	0.029916
8	1	0	-0.433453	-2.143838	-0.225525
9	1	0	-2.885499	-1.896595	-0.082561
10	1	0	-2.424216	2.380806	0.179682
11	6	0	-5.064034	-0.563432	0.124998
12	1	0	-4.894331	-1.240170	0.971390
13	1	0	-6.053781	-0.113121	0.210221
14	1	0	-4.994110	-1.120794	-0.817126
15	8	0	1.925971	-1.396281	-0.226850
16	8	0	-4.144859	0.526983	0.146562
17	6	0	1.443251	-0.278261	-0.192575
18	6	0	2.367659	0.975631	-0.215889
19	1	0	2.002420	1.685393	-0.964310
20	1	0	2.310759	1.441839	0.780784
21	7	0	3.736561	0.681752	-0.553991
22	7	0	5.301460	-0.642945	0.440543
23	7	0	4.372292	0.081224	0.578022

3.24. TS and IRC to form nitrene 10 from T_A of 1

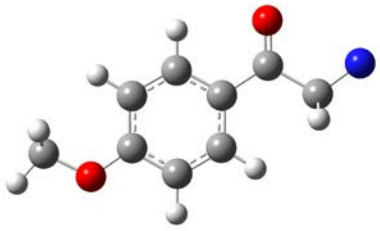


DFT/UB3LYP 6-31+G(d), E = -662.95041240 a.u.
Imaginary frequency = 1
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.597335	1.240976	-0.004168
2	6	0	-0.020646	-0.038703	-0.133091
3	6	0	-0.873390	-1.153984	-0.159693
4	6	0	-2.254812	-1.013267	-0.063248
5	6	0	-2.812508	0.269898	0.066076
6	6	0	-1.971923	1.396653	0.096004
7	1	0	0.024635	2.130603	0.024921
8	1	0	-0.431800	-2.141007	-0.255995
9	1	0	-2.882707	-1.896584	-0.088455
10	1	0	-2.421896	2.379253	0.198358
11	6	0	-5.060056	-0.566485	0.149526
12	1	0	-4.881388	-1.248388	0.989914
13	1	0	-6.049259	-0.117551	0.247464
14	1	0	-4.999212	-1.117918	-0.796724
15	8	0	1.926832	-1.391482	-0.279083
16	8	0	-4.141570	0.524494	0.168761
17	6	0	1.444086	-0.274048	-0.228107
18	6	0	2.366104	0.981451	-0.251119
19	1	0	2.004335	1.684326	-1.009152
20	1	0	2.296593	1.458692	0.739721
21	7	0	3.738165	0.694801	-0.573346
22	7	0	5.291923	-0.645355	0.512862
23	7	0	4.361551	0.057631	0.631834


Total Energy along IRC
Total Energy (Hartree)
-662.950
-662.955
-662.960
-662.965
-662.970
-662.975
-662.980
-662.985
-662.990
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Intrinsic Reaction Coordinate

3.25. Optimization of triplet nitrene 10



DFT/UB3LYP 6-31+G(d), E = -553.47344578 a.u.
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.236680	-1.186414	0.000065
2	6	0	-0.762132	0.121500	0.000028
3	6	0	0.138484	1.198536	-0.000030
4	6	0	1.515750	0.994263	-0.000052
5	6	0	2.021217	-0.316482	-0.000005
6	6	0	1.133243	-1.406142	0.000055
7	1	0	-0.895438	-2.049509	0.000115
8	1	0	-0.262591	2.207373	-0.000056
9	1	0	2.180676	1.850486	-0.000102
10	1	0	1.542656	-2.411611	0.000093
11	6	0	4.305865	0.417569	-0.000065
12	1	0	4.211646	1.041323	0.897411
13	1	0	5.277982	-0.077218	-0.000050
14	1	0	4.211632	1.041244	-0.897594
15	8	0	-2.648278	1.564519	0.000158
16	8	0	3.341964	-0.632946	-0.000011
17	6	0	-2.220858	0.423035	0.000079
18	6	0	-3.201152	-0.784541	0.000088
19	1	0	-2.987054	-1.411972	-0.885373
20	1	0	-2.987499	-1.411493	0.886001
21	7	0	-4.571989	-0.428450	-0.000372